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Abstract

Underground coal bed reservoirs naturally contain methane which can be produced. In parallel of the production of this methane, carbon dioxide can be injected, either to enhance the production of methane, or to have this carbon dioxide stored over geological periods of time. As a prerequisite to any simulation of an Enhanced Coal Bed Methane recovery process (ECBM), we need state equations to model the behavior of the seam when cleats are saturated with a miscible mixture of CH_4 and CO_2. This paper presents a poromechanical model of coal seams exposed to such binary mixtures filling both the cleats in the seam and the porosity of the coal matrix. This model is an extension of a previous work which dealt with pure fluid. Special care is dedicated to keep the model consistent thermodynamically. The model is fully calibrated with a mix of experimental data and numerical data from molecular simulations. Predicting variations of porosity or permeability requires only calibration based on swelling data. With the calibrated state

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equations, we predict numerically how porosity, permeability, and adsorbed amounts of fluid vary in a representative volume element of coal seam in isochoric or oedometric conditions, as a function of the pressure and of the composition of the fluid in the cleats.

Keywords:
poromechanics, competitive adsorption, coal swelling, binary mixtures

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1. Introduction

Coal seams are fractured porous media characterized by a relatively large internal surface area of about 30 $m^2.g^{-1}$ to 300 $m^2.g^{-1}$ [1]. Significant amounts of methane (CH_4) are generated and retained during the geological process leading to their formation, the so-called coalification process [2, 3]. Such coal bed methane (CBM) can be recovered from the coal seam and used for energy production. Conventional primary recovery of methane (called CBM production), which is performed by pumping out water and depressurizing the reservoir, allows producing 20% to 60% of the methane originally present in the reservoir [4]. As is the case with enhanced oil recovery (EOR), such primary production could be in principle enhanced by injecting CO_2 in the coal seam: this process is called CO_2-Enhanced Coal Bed Methane (CO_2-ECBM) recovery [4]. Thus, during CO_2-Enhanced Coal Bed Methane recovery, methane is produced while carbon dioxide is injected. An accurate description of the mixture of CH_4/CO_2 in the coal seam is essential for the development of reliable reservoir simulators used to history match field test data obtained from ECBM field tests [5].

Coal seams are naturally fractured by so-called cleats, the opening of which is usually smaller than 0.1 mm at surface conditions [6]. The spacing between those cleats is generally on the order of centimeters [6]. Although the cleat system often occupies less than 1% of the volume of coal [7], this system governs the permeability of the coal seam. Therefore, variations of cleat aperture lead to variations of permeability, which need to be modeled as accurately as possible. In-between those cleats, one finds the coal matrix (see Fig. 1), which itself is porous, as it contains both mesopores (i.e., pores with a diameter comprised between 2 nm and 50 nm) and micropores (i.e., pores with a diameter smaller than 2 nm). In such small pores, a significant amount of molecules of the pore fluid are in intermolecular interactions with the atoms of the solid skeleton: those molecules are said to be adsorbed. Adsorption confers some specific poromechanical features to the coal matrix: in particular, one observes that coal, when immersed in fluids that can be adsorbed (for instance carbon dioxide or methane), swells [8]. This adsorption-induced deformation of the coal matrix leads to variations of the aperture of cleats, which itself translates into variations of permeability of the coal seam. During CO_2-Enhanced Coal Bed Methane recovery, variations of permeability result therefore from the combination of regular poromechanical effects induced by variations of fluid pressure in the macroporous cleats with adsorption-induced deformations of the coal matrix [9]. Various authors aimed at introducing adsorption-induced swelling effects in coal modeling (for reviews, see [10] and [11]).

Deformations induced by adsorption were observed and studied in a variety of materials, either mesoporous (e.g., porous silicon [12, 13] or meso-

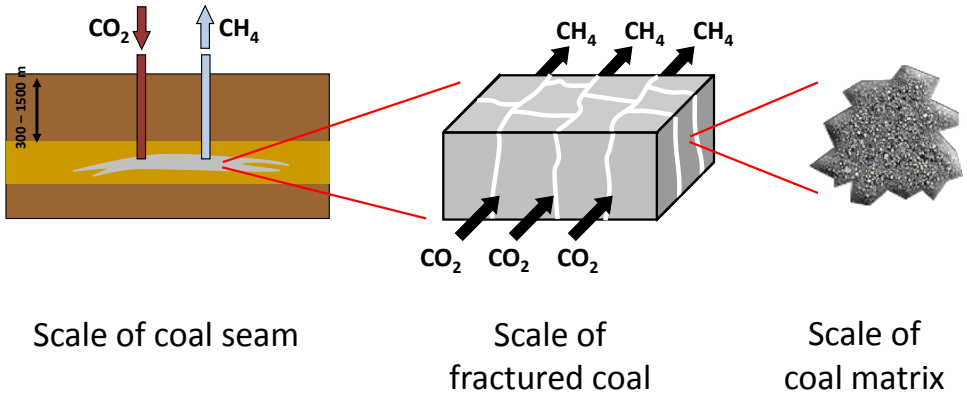


Figure 1: Various scales introduced.

porous silica [14, 15, 16, 17]) or microporous (e.g., metal-organic frameworks [18, 19], zeolites [20], microporous carbons or coal [21, 22, 23]). In mesoporous solids, adsorption is mostly a surface phenomenon, with adsorbed molecules located at the surface of the pores. In contrast, in microporous solids, the very notion of pore surface breaks down and adsorption occurs by micropore filling rather than by surface covering. The reverse coupling between adsorption and strain (i.e., the fact that strain or stress can modify the adsorption process) was also observed. For instance, Grosman and Ortega [24, 12] showed the influence of the elastic deformation of porous solids on the adsorption process: a stress external to the porous layer can modify the adsorbed amount. Finally, this coupling between strain and adsorption was also studied for fluid mixtures, for instance in the case of adsorption of binary mixtures in metal-organic frameworks [25].

Based on field and laboratory experimental results, a large variety of permeability relations has been proposed for coal seams (for reviews, see [10] and

[11]), starting with the work of Gray [26]. Some models derive such relations by using porosity as an intermediate variable parameter (e.g., [27, 28]) while, in contrast, other models are stress-based (e.g., [29]). Relations were derived for various conditions (e.g., oedometric conditions [28], variable stress conditions [30], or triaxial strain or stress conditions [31]). Some models were based on some specific geometries (e.g., a matchstick geometry [32]), or were instead derived for more general geometries by starting from the equations of poroelasticity (e.g., [33]). Liu and Rutqvist [34] considered interaction between adjacent coal matrix blocks through coal matrix bridges. Recently, Liu et al. [35] considered the effect of the transient transfer of fluid between cleats and coal matrix, and Wu et al. [36] derived a poroelastic model aiming at capturing the interactions between binary fluid mixtures (CH_4 and CO_2) and the dual-porosity medium (coal matrix and cleats).

Therefore, a large variety of coal models has been developed (for reviews, see [10] and [11]). All these models were derived from the theory of poroelasticity or from more empirical continuum approaches. But, while those models focus on how adsorption leads to swelling, only a minority considers the reverse coupling, i.e, how swelling or stresses can modify adsorption, while the fact that compressive stresses can lead to desorption in coal has been shown experimentally [37]. When models do consider such reverse coupling (e.g., [38, 22, 39]), they do so by introducing a pore volume of the coal matrix, although defining or measuring the pore volume of a microporous solid such as coal in an unambiguous manner is not possible, since its apparent pore volume depends for instance on the fluid with which this pore volume is probed [40]. In contrast, here, we aim at deriving a model with a

thermodynamical basis to capture this strong coupling between adsorption and swelling, without introducing an ill-defined notion of porosity or of pore volume for the coal matrix: our model is only based on well-defined quantities. Here, a dual-porosity model, based on the Biot-Coussy poromechanical framework [41], is proposed for the behavior of a representative volume element of coal bed reservoir. Both the porous networks of the cleats of the seam and of the coal matrix are explicitly taken into account, but we never introduce the pore volume or the porosity of the coal matrix. The resulting state equations require directly as an input the adsorption isotherms of the fluids considered on coal and data on adsorption-induced swellings. Recently, we developed a dual-porosity model for coal bed reservoirs, that considered adsorption in the coal matrix as a surface phenomenon [42, 43]. In contrast, we then developed a model for coal bed reservoirs that also considered the microporosity of the coal matrix [44], in which adsorption occurs by pore filling rather than by surface covering. In fact, this latter model is valid for a coal matrix with a generic pore size distribution. However, this latter dual-porosity poromechanical model only holds for media saturated with a pure fluid.

During ECBM, as the coal bed reservoirs initially contain methane, the injection of carbon dioxide induces a progressive replacement of methane with carbon dioxide. Therefore, here, we develop a dual-porosity model for media exposed to binary mixtures of fluids. We aim at deriving poromechanical equations that model the coupling between adsorption and strains/stresses, and thus enable to predict how the replacement of methane with carbon dioxide leads to strains and variations of porosity or permeability.

2. Description of the case considered

A representative volume element of coal seam is made of cleats (i.e., macropores) and of a coal matrix which is potentially microporous (see Fig. 1), thus defining two scales: the scale of fractured coal (i.e., a representative volume element of coal seam), and that of the coal matrix.

The elastic behavior of the reservoir is considered to be linear and isotropic. Only small strains are considered. The pore space is filled with methane and carbon dioxide, which are assumed to be miscible. The fluid in the cleats is considered to be in a bulk state. Molecules of fluid can be found not only in the cleats, but also in the coal matrix. We assume that fluids in the cleats and in the coal matrix are in equilibrium at all times: the kinetics associated to a transfer of fluid from the cleats to the coal matrix is assumed to be much faster than any other kinetics of the process. Note however that, during the derivation of the state equations, the pressure p of the fluid in the cleats will be considered to be different from the thermodynamic pressure of the fluid in the coal matrix: those two pressures will only be equated at the end of the derivation. Thus, for the derivation, the molar chemical potentials of methane and carbon dioxide in the coal matrix will be considered to differ from the molar chemical potentials of methane and carbon dioxide in the cleats.

The bulk mixture of fluid in the cleats is characterized by its pressure p and by its mole fraction $x^{\mathrm{CO_2}}$ of carbon dioxide. Alternatively, the state of the fluid in the cleats can be defined through the fugacities $f^{\mathrm{CH_4}}$ of methane and $f^{\mathrm{CO_2}}$ of carbon dioxide, i.e., $p = p(f^{\mathrm{CO_2}}, f^{\mathrm{CH_4}})$ and $x^{\mathrm{CO_2}} = x^{\mathrm{CO_2}}(f^{\mathrm{CO_2}}, f^{\mathrm{CH_4}})$.

If we were to consider a nonporous coal matrix, i.e., with no adsorption

effect, the coal seam could be considered as a regular macroporous medium made of one pore network (i.e., the network of cleats). Therefore, the energy balance for the nonporous coal matrix in a representative volume element of coal seam would be [41]:

$$df = \sigma d\epsilon + s_{ij} de_{ij} + p d\phi \tag{1}$$

where f is the Helmholtz free energy of the coal matrix per unit volume of coal seam, σ is the volumetric stress, ϵ is the volumetric strain, s_{ij} are the deviatoric stresses, e_{ij} are the deviatoric strains, and ϕ is the Lagrangian porosity of the cleats. Based on this energy balance, one can write the state equations of the coal seam in absence of any adsorption effect (i.e., for a nonporous coal matrix) as [41]:

$$d\sigma = (K + b^2 N) d\epsilon - bN d\phi \tag{2}$$

$$dp = -bN d\epsilon + N d\phi \tag{3}$$

$$ds_{ij} = 2G de_{ij} \tag{4}$$

where K is the drained compression modulus, b is the Biot's coefficient, N is the Biot's modulus and G the shear modulus [41].

3. Insertion of adsorption effects: case of coal saturated with a pure fluid

We now consider a porous coal matrix in contact with a pure fluid: adsorption effects can occur within this matrix. For such coal matrix within a representative volume element of coal seam, the energy balance is:

$$df = \sigma d\epsilon + s_{ij} de_{ij} + p d\phi + \mu dn, \tag{5}$$

where n is the molar fluid content in the coal matrix (i.e., not in the cleats) per unit volume of undeformed coal seam and μ is the chemical potential of fluid in the coal matrix. Making use of a Legendre-Fenchel transform, this energy balance can be rewritten as:

$$d(f - n\mu) = \sigma d\epsilon + s_{ij} de_{ij} + p d\phi - n d\mu, \tag{6}$$

from which the state equations in presence of adsorption effects can be inferred in a differential form:

$$\begin{aligned} d\sigma &= (K + b^2 N) d\epsilon - bN d\phi + \alpha_1 d\mu & (7)\\ dp &= -bN d\epsilon + N d\phi + \alpha_2 d\mu & (8)\\ ds_{ij} &= 2G de_{ij} & (9)\\ dn &= -\alpha_1 d\epsilon - \alpha_2 d\phi + \alpha_3 d\mu & (10) \end{aligned}$$

where the functions α_1 to α_3 need to be determined. The amount n of fluid in the coal matrix depends on the chemical potential μ of the fluid in the coal matrix and on the volume strain ϵ_m of the coal matrix. Using classical micromechanical relations [41], this volume strain of the coal matrix can be related to the volume strain ϵ of the coal seam and to the porosity ϕ of the cleats through:

$$\epsilon = (1 - \phi_0)\epsilon_m + \phi - \phi_0 \tag{11}$$

$$\epsilon_m = \frac{\epsilon - (\phi - \phi_0)}{1 - \phi_0} \tag{12}$$

where ϕ_0 is the porosity of the cleats in the state of reference.

In addition, since small strains are considered, we can approximate the adsorbed amount by a first-order expansion with respect to the volume strain ϵ_m of the coal matrix:

$$n(\mu, \epsilon_m) = (1 - \phi_0)\left[n_0(\mu) + a(\mu)\epsilon_m\right] \tag{13}$$

where $n_0 + a\epsilon_m$ is the adsorption isotherm per unit volume of undeformed coal matrix, and where n_0 is the adsorption isotherm on a rigid coal matrix. Brochard et al. [45] showed by molecular simulations that such expansion is valid for adsorption of methane in coal for volumetric strains of coal up to 10 %. With this first-order expansion of the adsorption isotherm with respect to the strain of the coal matrix, we find out that:

$$\alpha_1 = -\left.\frac{\partial n}{\partial \epsilon}\right|_{\phi,\mu} = -(1 - \phi_0)a \left.\frac{\partial \epsilon_m}{\partial \epsilon}\right|_{\phi} = -a \tag{14}$$

so that $\alpha_1 = -a(\mu)$. Likewise, we find out that:

$$\alpha_2 = -\left.\frac{\partial n}{\partial \phi}\right|_{\epsilon,\mu} = -(1 - \phi_0)a \left.\frac{\partial \epsilon_m}{\partial \phi}\right|_{\epsilon} = a \tag{15}$$

so that $\alpha_2 = -\alpha_1 = a(\mu)$.

We note $ad\mu$ as ds^a, where s^a is the volumetric part of an adsorption stress (from now on referred to as an 'adsorption stress') [20, 46], and depends only

on the chemical potential of the fluid: $s^a = s^a(\mu)$. Finally, in a differential form the state equations in presence of adsorption effects are:

$$d\sigma = (K + b^2 N)d\epsilon - bNd\phi - ds^a \quad (16)$$

$$dp = -bNd\epsilon + Nd\phi + ds^a \quad (17)$$

$$ds_{ij} = 2Gde_{ij} \quad (18)$$

where the small increment ds^a of adsorption stress is given by:

$$ds^a = ad\mu. \quad (19)$$

In addition the amount n of fluid in the coal matrix is governed by the adsorption isotherm (13).

It should be noted that this approach does not refer to any particular size of pores. Unlike cleats, the coal matrix here considered could contain micropores smaller than 2 nm, the volume of which is ill-defined. Our approach is then suited for a porous solid with a generic pore size distribution. The model relies only on the assumed knowledge of the adsorption isotherm, without referring explicitly to a pore volume or to a pore size distribution. The apparent density of the adsorbed fluid is likely to differ from the density ρ of the bulk fluid. It is therefore not possible to assert, as was done for cleats, that the adsorbed fluid occupies a volume n/ρ in the coal matrix. Indeed, for very small pores, the apparent density of the adsorbed fluid can differ significantly from ρ, so that the volume n/ρ can differ significantly from that of the accommodating coal sample. Therefore, the pore size distribution of the coal matrix is expected to impact strongly the adsorbed amount n, the

coupling coefficient a and thus the adsorption stress s^a.

4. Insertion of adsorption effects: case of coal saturated with a mixture of two miscible fluids

We now consider that the coal seam is saturated with a mixture of two miscible fluids: the coal matrix will therefore adsorb a mixture of both fluids. The energy balance for the coal matrix in a representative volume element of coal seam is now:

$$df = \sigma d\epsilon + p d\phi + s_{ij} de_{ij} + \mu^{\mathrm{CH_4}} dn^{\mathrm{CH_4}} + \mu^{\mathrm{CO_2}} dn^{\mathrm{CO_2}}, \tag{20}$$

where $n^{\mathrm{CH_4}}$ and $n^{\mathrm{CO_2}}$ are the amount of methane and carbon dioxide in the coal matrix per unit volume of coal seam, respectively; and where $\mu^{\mathrm{CH_4}}$ and $\mu^{\mathrm{CO_2}}$ are the molar chemical potential of methane and carbon dioxide in the coal matrix, respectively. Making use of a Legendre-Fenchel transform, this energy balance can be rewritten as:

$$d(f - n^{\mathrm{CH_4}}\mu^{\mathrm{CH_4}} - n^{\mathrm{CO_2}}\mu^{\mathrm{CO_2}}) = \sigma d\epsilon + s_{ij} de_{ij} + p d\phi - n^{\mathrm{CH_4}} d\mu^{\mathrm{CH_4}} - n^{\mathrm{CO_2}} d\mu^{\mathrm{CO_2}}, \tag{21}$$

from which the state equations for a coal seam saturated with a mixture of two fluids can be inferred in a differential form:

$$
\begin{aligned}
d\sigma &= (K + b^2 N)d\epsilon - bNd\phi + \alpha_4 d\mu^{\mathrm{CH_4}} + \alpha_5 d\mu^{\mathrm{CO_2}} && (22)\\
dp &= -bNd\epsilon + Nd\phi + \alpha_6 d\mu^{\mathrm{CH_4}} + \alpha_7 d\mu^{\mathrm{CO_2}} && (23)\\
dn^{\mathrm{CH_4}} &= -\alpha_4 d\epsilon - \alpha_6 d\phi + \alpha_8 d\mu^{\mathrm{CH_4}} + \alpha_9 d\mu^{\mathrm{CO_2}} && (24)\\
dn^{\mathrm{CO_2}} &= -\alpha_5 d\epsilon - \alpha_7 d\phi + \alpha_9 d\mu^{\mathrm{CH_4}} + \alpha_{10} d\mu^{\mathrm{CO_2}} && (25)\\
ds_{ij} &= 2Gde_{ij}, && (26)
\end{aligned}
$$

where the functions α_4 to α_{10} need to be determined.

Since strains are small, we can approximate the adsorbed amounts by a first-order expansion with respect to the volume strain ϵ_m of the coal matrix:

$$
\begin{aligned}
n^{\mathrm{CH_4}}(\epsilon_m, \mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}}) &= (1-\phi_0)\left(n_0^{\mathrm{CH_4}} + a^{\mathrm{CH_4}}\epsilon_m\right) && (27)\\
n^{\mathrm{CO_2}}(\epsilon_m, \mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}}) &= (1-\phi_0)\left(n_0^{\mathrm{CO_2}} + a^{\mathrm{CO_2}}\epsilon_m\right), && (28)
\end{aligned}
$$

where the functions $n_0^{\mathrm{CH_4}}(\mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}})$, $n_0^{\mathrm{CO_2}}(\mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}})$, $a^{\mathrm{CH_4}}(\mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}})$, and $a^{\mathrm{CO_2}}(\mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}})$ all are functions of the chemical potentials only, and where the volume strain ϵ_m of the coal matrix is still related to the porosity ϕ of the cleats and to the volume strain ϵ of the coal seam with Eq. (12). $n_0^{\mathrm{CH_4}} + a^{\mathrm{CH_4}}\epsilon_m$ and $n_0^{\mathrm{CO_2}} + a^{\mathrm{CO_2}}\epsilon_m$ are the adsorption isotherms of methane and carbon dioxide per unit volume of undeformed coal matrix, respectively. $n_0^{\mathrm{CH_4}}$ and $n_0^{\mathrm{CO_2}}$ are the adsorption isotherms of methane and carbon dioxide on a rigid coal matrix, respectively. With these first-order expansions of the adsorption isotherms, we find out that:

$$
\alpha_4 = -\left.\frac{\partial n^{\mathrm{CH_4}}}{\partial \epsilon}\right|_{\phi,\mu^{\mathrm{CH_4}},\mu^{\mathrm{CO_2}}} = -(1-\phi_0)a^{\mathrm{CH_4}}\left.\frac{\partial \epsilon_m}{\partial \epsilon}\right|_{\phi} = -a^{\mathrm{CH_4}}, \qquad (29)
$$

so that $\alpha_4 = -a^{\mathrm{CH_4}}(\mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}})$. Likewise, we find out that:

$$\alpha_6 = -\left.\frac{\partial n^{\mathrm{CH_4}}}{\partial \phi}\right|_{\epsilon,\mu^{\mathrm{CH_4}},\mu^{\mathrm{CO_2}}} = -(1-\phi_0)a^{\mathrm{CH_4}}\left.\frac{\partial \epsilon_m}{\partial \phi}\right|_{\epsilon} = a^{\mathrm{CH_4}}, \tag{30}$$

so that $\alpha_6 = -\alpha_4 = a^{\mathrm{CH_4}}(\mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}})$.

We also find out that:

$$\alpha_5 = \alpha_5(\mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}}) = -a^{\mathrm{CO_2}} \tag{31}$$

$$\alpha_7 = \alpha_7(\mu^{\mathrm{CH_4}}, \mu^{\mathrm{CO_2}}) = a^{\mathrm{CO_2}}. \tag{32}$$

The function $a^{\mathrm{CH_4}}d\mu^{\mathrm{CH_4}} + a^{\mathrm{CO_2}}d\mu^{\mathrm{CO_2}}$ can be rewritten as a small increment ds^a of adsorption stress:

$$ds^a = a^{\mathrm{CH_4}}d\mu^{\mathrm{CH_4}} + a^{\mathrm{CO_2}}d\mu^{\mathrm{CO_2}}, \tag{33}$$

which was inferred from the Maxwell symmetry relationship derived from Eq. (22):

$$-\frac{\partial^2 \sigma}{\partial \mu^{\mathrm{CH_4}} \partial \mu^{\mathrm{CO_2}}} = \left.\frac{\partial a^{\mathrm{CH_4}}}{\partial \mu^{\mathrm{CO_2}}}\right|_{\mu^{\mathrm{CH_4}}} = \left.\frac{\partial a^{\mathrm{CO_2}}}{\partial \mu^{\mathrm{CH_4}}}\right|_{\mu^{\mathrm{CO_2}}}. \tag{34}$$

In such a case, finally, in a differential form the state equations of a coal seam in presence of a binary mixture of fluids are:

$$d\sigma = (K + b^2 N)d\epsilon - bNd\phi - ds^a \tag{35}$$

$$dp = -bNd\epsilon + Nd\phi + ds^a \tag{36}$$

$$ds_{ij} = 2Gde_{ij} \tag{37}$$

where the small increment ds^a of adsorption stress is given by:

$$ds^a = a^{\mathrm{CH_4}} d\mu^{\mathrm{CH_4}} + a^{\mathrm{CO_2}} d\mu^{\mathrm{CO_2}} \tag{38}$$

In addition the amounts $n^{\mathrm{CH_4}}$ and $n^{\mathrm{CO_2}}$ of fluid in the coal matrix are given by Eqs. (27)-(28), respectively.

As was the case for a coal seam saturated with a pure fluid, adsorption effects for a coal seam saturated with a mixture of two miscible fluids can be captured by the introduction of an adsorption stress s^a. Moreover, one notes that the state equations (35)-(37) derived for a coal seam saturated with a mixture of two miscible fluids are strictly identical to the state equations (16)-(18) derived for a coal seam saturated with a pure fluid. However, while a small increment ds^a of adsorption stress is given by Eq. (19) when coal is saturated with a pure fluid, this same small increment ds^a is given by Eq. (38) when coal is saturated with a mixture of two miscible fluids. Let us point out that this result is obtained without referring to an ideality of the mixture of CH_4 and CO_2 since the chemical potentials of these gases in the mixture are general and do not refer to any specific model. However, the derivation of the adsorption stress, as resulting from a total exact differential form, relies on the assumption that the gas contents are linearly linked to the strain (see Eqs. (27) and (28)).

Thermodynamic equilibrium of each fluid found in the cleats and in the coal matrix is now introduced. Equating the chemical potentials in differential form yields:

$$d\mu^{\mathrm{CH_4}} = RT\frac{df^{\mathrm{CH_4}}}{f^{\mathrm{CH_4}}} \tag{39}$$

$$d\mu^{\mathrm{CO_2}} = RT\frac{df^{\mathrm{CO_2}}}{f^{\mathrm{CO_2}}}, \tag{40}$$

with T the temperature and R the ideal gas constant, so that, eventually, $\mu^{\mathrm{CH_4}} = \mu^{\mathrm{CH_4}}(f^{\mathrm{CH_4}}) = \mu^{\mathrm{CH_4}}(p, x^{\mathrm{CO_2}})$ and $\mu^{\mathrm{CO_2}} = \mu^{\mathrm{CO_2}}(f^{\mathrm{CO_2}}) = \mu^{\mathrm{CO_2}}(p, x^{\mathrm{CO_2}})$.

5. Application to coal saturated with a mixture of $\mathbf{CH_4}$ and $\mathbf{CO_2}$

Based on the derivations performed in the previous section, one can predict how various parameters such as cleat porosity or permeability evolve for a representative volume element of coal seam saturated by a mixture of two fluids, as will be explained in Sec. 5.2. In addition, a salient feature of our model is that it captures the full coupling between adsorption and stresses/strains: not only does it make it possible to predict how stresses or strains evolve in presence of adsorption, but also does it make it possible to predict how stresses or strains affect adsorption, as will be presented in the section after. As a prerequisite to those calculations, the adsorption stress s^a that develops when cleats are occupied by a mixture of fluids must be calculated, which is the focus of the next section.

The properties of the coal here considered are given in Table 1. All properties are characteristic of coal.

5.1. Calculation of adsorption stress

This section is dedicated to calculating the adsorption stress s^a for a specific coal. Since the cleat porosity is occupied by a mixture of methane

Table 1: Parameters of the coal of interest. For values not provided by Pini et al. [47], a typical range of values is indicated. Values from a) [47], b) [48], c) [7], d) [49], e) [50]. The bulk modulus K_m of the coal matrix and the Biot modulus N are calculated with the following relations [41]: $b = 1 - K/K_m$ and $1/N = (b - \phi_0)/K_m$.

Property	Definition, Unit	Value	Typical range of values
K	Bulk modulus of coal sample, GPa	0.78[a)]	
b	Biot coefficient of coal sample	0.75	[0:1][b)]
K_m	Bulk modulus of coal matrix, GPa	3.12	
ϕ_0	Initial porosity of cleats	3.2%[a)]	
N	Biot modulus, GPa	4.22	
γ	Pressure sensitivity parameter, MPa^{-1}	0.15	[0.04[d)]:0.9[e)]]

and carbon dioxide, this adsorption stress depends on both the pressure p of the mixture in the cleats and on the mole fraction $x^{\mathrm{CO_2}}$ of carbon dioxide in this mixture, i.e.:

$$s^a(p, x^{\mathrm{CO_2}}) = s^a(f^{\mathrm{CH_4}}, f^{\mathrm{CO_2}}) \tag{41}$$

where $f^{\mathrm{CH_4}}$ and $f^{\mathrm{CO_2}}$ are the fugacities of methane and carbon dioxide in the mixture that saturates the cleats, respectively. Since we assume thermodynamic equilibrium between cleats and coal matrix, those fugacities are also those of methane and carbon dioxide in the coal matrix. However, because of adsorption, the mole fraction of carbon dioxide in the coal matrix is likely to differ from the mole fraction $x^{\mathrm{CO_2}}$ of carbon dioxide in the cleats [45].

We first perform some simplification, while aiming at keeping the thermodynamic consistency of the model, i.e., at being consistent with the following equation obtained by a combination of Eq. (38) with Eqs. (39)-(40):

$$ds^a = RT\left[a^{\mathrm{CH_4}}\frac{df^{\mathrm{CH_4}}}{f^{\mathrm{CH_4}}} + a^{\mathrm{CO_2}}\frac{df^{\mathrm{CO_2}}}{f^{\mathrm{CO_2}}}\right]. \tag{42}$$

From the lack of knowledge, we assume that the coefficients $a^{\mathrm{CH_4}}$ and $a^{\mathrm{CO_2}}$ are of the form:

$$a^{\mathrm{CH_4}}(p, x^{\mathrm{CO_2}}) = a^{\mathrm{CH_4}}(f^{\mathrm{CH_4}}) \tag{43}$$

$$a^{\mathrm{CO_2}}(p, x^{\mathrm{CO_2}}) = a^{\mathrm{CO_2}}(f^{\mathrm{CO_2}}). \tag{44}$$

With such an assumption, the compatibility equation (34) is readily enforced, which enables to ensure that the thermodynamic consistency of the model is conserved.

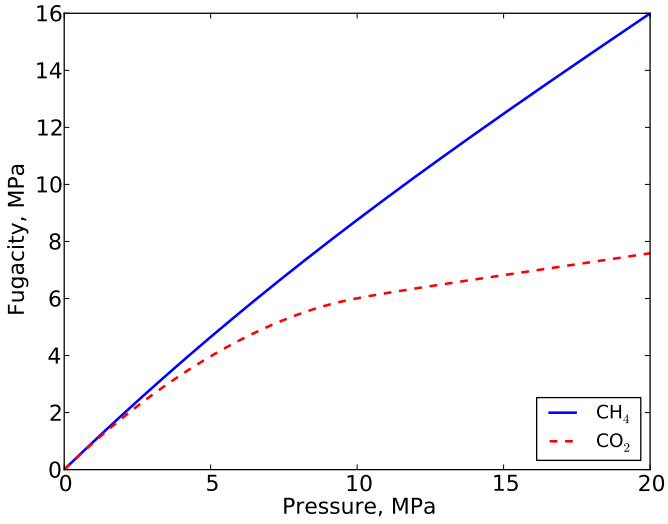
The fugacities of pure methane and pure carbon dioxide are noted $f_*^{\mathrm{CH_4}}$ and $f_*^{\mathrm{CO_2}}$, respectively. Those fugacities, calculated from the NIST thermophysical properties of fluid systems (http://webbook.nist.gov/chemistry/), are displayed in Fig. 2a. From molecular simulations of bulk binary mixtures of methane and carbon dioxide [45] (see Fig. 2b), one observes that, in first-order approximation, the fugacities $f^{\mathrm{CO_2}}$ of carbon dioxide and $f^{\mathrm{CH_4}}$ of methane in the mixture can be linked to the fugacities $f_*^{\mathrm{CO_2}}$ of pure carbon dioxide and $f_*^{\mathrm{CH_4}}$ of pure methane at the same pressure as the mixture through:

$$f^{\mathrm{CH_4}} = f_*^{\mathrm{CH_4}}\left(1 - x^{\mathrm{CO_2}}\right) \tag{45}$$

$$f^{\mathrm{CO_2}} = f_*^{\mathrm{CO_2}} x^{\mathrm{CO_2}}. \tag{46}$$

Those equations state that the binary mixture follows a Raoult's law, i.e., that the chemical potentials of methane and carbon dioxide in the mixture

(a)



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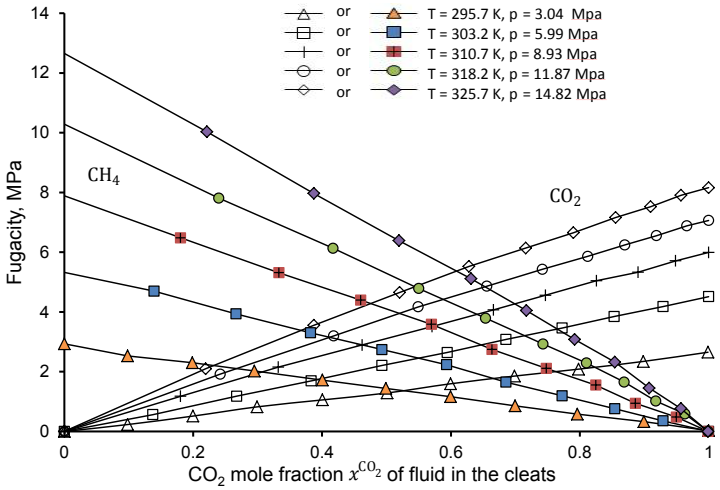
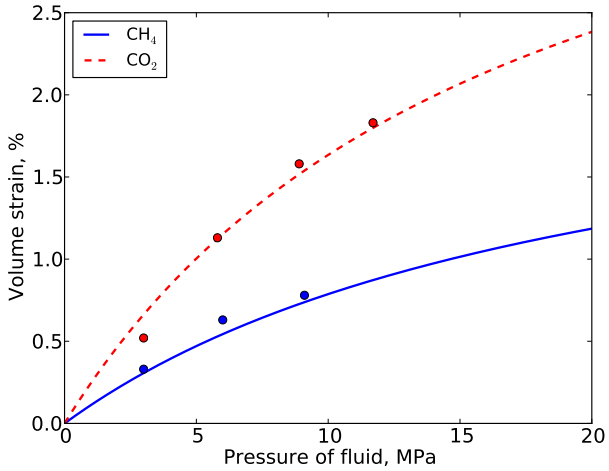


Figure 2: (a) Fugacity $f_*^{\mathrm{CO_2}}$ of pure carbon dioxide and $f_*^{\mathrm{CH_4}}$ of pure methane at a temperature $T = 318.15$ K, adapted from the NIST thermophysical properties of fluid systems (http://webbook.nist.gov/chemistry/). (b) Fugacity $f^{\mathrm{CH_4}}$ of methane and $f^{\mathrm{CO_2}}$ of carbon dioxide in the CH_4-CO_2 mixture, as a function of the pressure, temperature and composition of the mixture, adapted from molecular simulations by Brochard et al. [45]. Open symbols are for CO_2 while filled symbols are for CH_4.

(a)



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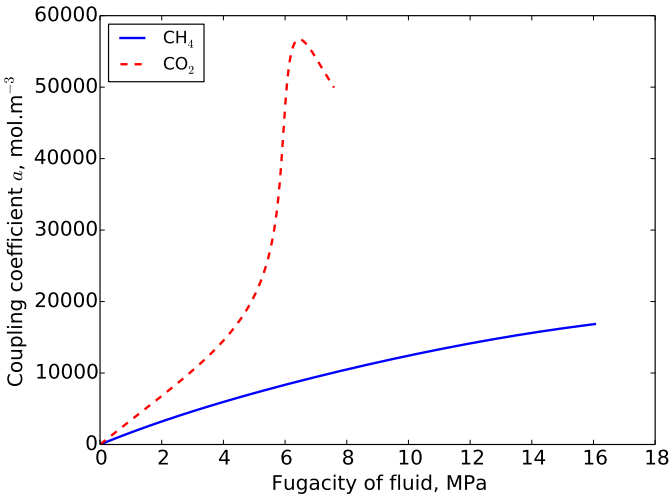


Figure 3: (a) Volume strain of Ribolla coal sample immersed in pure methane or pure carbon dioxide at a temperature $T = 318.15$ K. Data is adapted from Pini et al. [51]. Symbols are data points while lines are models fitted by Pini et al. on their data. (b) Functions $a^{\mathrm{CH_4}}$ and $a^{\mathrm{CO_2}}$ that govern how strain modifies adsorption (see Eqs. (27)-(28)).

are given by $\mu^{CH_4} = \mu_*^{CH_4} + RT\ln(1-x^{CO_2})$ and $\mu^{CO_2} = \mu_*^{CO_2} + RT\ln(x^{CO_2})$. The bulk mixture is therefore assumed as ideal here. This assumption is supported by observations in a first approximation as shown in Fig. 2, even though a more accurate observation of these curves shows a slight departure from ideality.

Under the above assumptions, we will show that the only data required to calculate the adsorption stress in presence of a mixture are data of swelling of coal samples in presence of the pure fluids. We will use swelling strains data obtained by Pini [51] for Ribolla coal in presence of pure methane or pure carbon dioxide at a temperature $T = 318.15$ K. Their data are displayed in Fig. 3a. The strains of coal samples immersed in pure methane or in pure carbon dioxide are noted ϵ^{CH_4} and ϵ^{CO_2}, respectively. Considering the state equations (16) and (17) for a sample immersed in a fluid (i.e., for which $\sigma = -p$), independently of the initial porosity ϕ_0 of the cleats, one finds out that the coupling coefficients a^{CH_4} and a^{CO_2} are linked to the measured swelling strains through:

$$a^{CH_4}\left(f_*^{CH_4}\right) = \rho^{CH_4}\left(1 + K_m\frac{d\epsilon^{CH_4}}{dp}\right) \text{ and } a^{CO_2}\left(f_*^{CO_2}\right) = \rho^{CO_2}\left(1 + K_m\frac{d\epsilon^{CO_2}}{dp}\right), \tag{47}$$

where ρ^{CH_4} and ρ^{CO_2} are the bulk densities of methane and carbon dioxide, respectively, and where K_m is the bulk modulus of the coal matrix. Thus, the functions $a^{CH_4}\left(f^{CH_4}\right)$ and $a^{CO_2}\left(f^{CO_2}\right)$ can be identified with the equations (47) derived for pure fluids. The results of those calculations based on the data obtained by Pini [51] are displayed in Fig. 3b. In this figure, the coupling coefficient obtained for CO_2 shows a peak resulting from the competition

between two contrasting behaviors. We can show that $a = \rho(ds^a/dp)$, where the gas density ρ is an increasing function of pressure, and where ds^a/dp is a decreasing function of pressure [44]. It turns out that the derivative of a with respect to fugacity is dominated by that of ρ for small pressures and by that of ds^a/dp for high pressures (actually supercritical pressures).

The functions $a^{\mathrm{CH_4}}$ and $a^{\mathrm{CO_2}}$ being now known, the adsorption stress s^a can be calculated with the help of Eq. (38):

$$ds^a(p, x^{\mathrm{CO_2}}) = a^{\mathrm{CH_4}} d\mu^{\mathrm{CH_4}} + a^{\mathrm{CO_2}} d\mu^{\mathrm{CO_2}} \quad (48)$$

$$= RT \left[\frac{a^{\mathrm{CH_4}}(f^{\mathrm{CH_4}})}{f^{\mathrm{CH_4}}} df^{\mathrm{CH_4}} + \frac{a^{\mathrm{CO_2}}(f^{\mathrm{CO_2}})}{f^{\mathrm{CO_2}}} df^{\mathrm{CO_2}} \right] \quad (49)$$

or, in an integrated form:

$$s^a(p, x^{\mathrm{CO_2}}) = RT \left[\int_0^{f^{\mathrm{CH_4}}} \frac{a^{\mathrm{CH_4}}(\tilde{f}^{\mathrm{CH_4}})}{\tilde{f}^{\mathrm{CH_4}}} d\tilde{f}^{\mathrm{CH_4}} + \int_0^{f^{\mathrm{CO_2}}} \frac{a^{\mathrm{CO_2}}(\tilde{f}^{\mathrm{CO_2}})}{\tilde{f}^{\mathrm{CO_2}}} d\tilde{f}^{\mathrm{CO_2}} \right] \quad (50)$$

$$= RT \left[\int_0^{f_*^{\mathrm{CH_4}} x^{\mathrm{CH_4}}} \frac{a^{\mathrm{CH_4}}(\tilde{f}^{\mathrm{CH_4}})}{\tilde{f}^{\mathrm{CH_4}}} d\tilde{f}^{\mathrm{CH_4}} + \int_0^{f_*^{\mathrm{CO_2}} x^{\mathrm{CO_2}}} \frac{a^{\mathrm{CO_2}}(\tilde{f}^{\mathrm{CO_2}})}{\tilde{f}^{\mathrm{CO_2}}} d\tilde{f}^{\mathrm{CO_2}} \right] \quad (51)$$

Here, the adsorption stress $s^a(p, x^{\mathrm{CO_2}})$ was calculated based on the experimental data obtained for pure methane and pure carbon dioxide on Ribolla coal at a temperature $T = 318.15$ K (see Fig. 3a) and on the fugacities of pure methane and pure carbon dioxide obtained from the NIST thermophysical properties of fluid systems (http://webbook.nist.gov/chemistry/) at the same temperature (see Fig. 2a). Fig. 4 displays the adsorption stress

$s^a(p, x^{CO_2})$ for various values of the mole fraction x^{CO_2} of carbon dioxide in the fluid mixture in the cleats and for various pressures p of this mixture. Fig. 4 shows that variations of the adsorption stress $s^a(p, x^{CO_2})$ are non trivial. This adsorption stress increases with the pressure p of the mixture in the cleats. The adsorption stress also increases with the mole fraction of carbon dioxide in a way depending on the pressure level. At low pressure the fugacities of the two gases are small enough for the coupling coefficient to be approximated by a first-order expansion of the fugacity. It turns out that the adsorption stress is linearly linked to the mole fraction. At high pressure, namely close to the critical point of CO_2, the coupling coefficient relative to CO_2 is no more linearly linked to the fugacity, as shown in Fig. 3b. As a consequence, the adsorption stress presents a nonlinear behavior for a large enough CO_2 mole fraction, as shown in Fig. 4b.

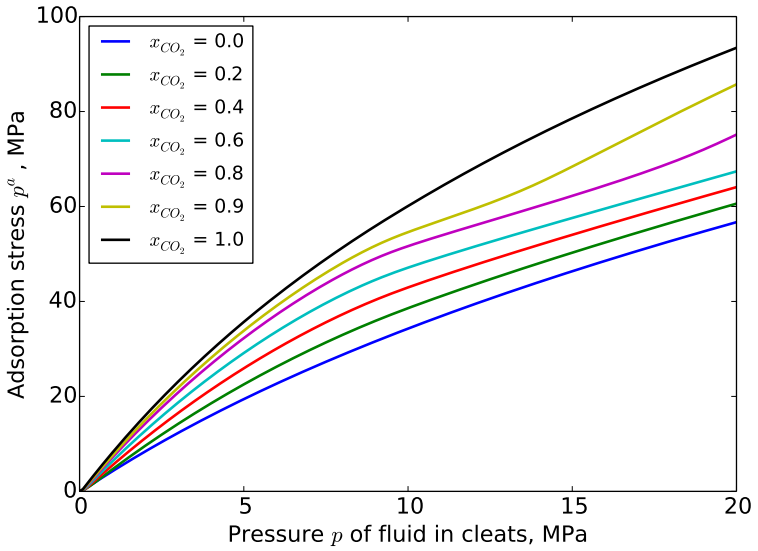
5.2. Prediction of variations of porosity and permeability for sample in isochoric conditions

The knowledge of this adsorption stress now makes it possible to use the state equations (35)-(37). In this section, we focus on a representative volume element of coal seam kept in isochoric conditions, i.e., $\epsilon = 0$. Among others, the state equations enable to calculate variations of porosity:

$$\phi - \phi_0 = \frac{1}{N}(p - s^a) \tag{52}$$

The calculated variations of porosity are displayed in Fig. 5. One observes that, in the range of pressures considered, for a given composition of the mixture in the cleats, any increase of pressure in the cleats translates into

(a)



(b)

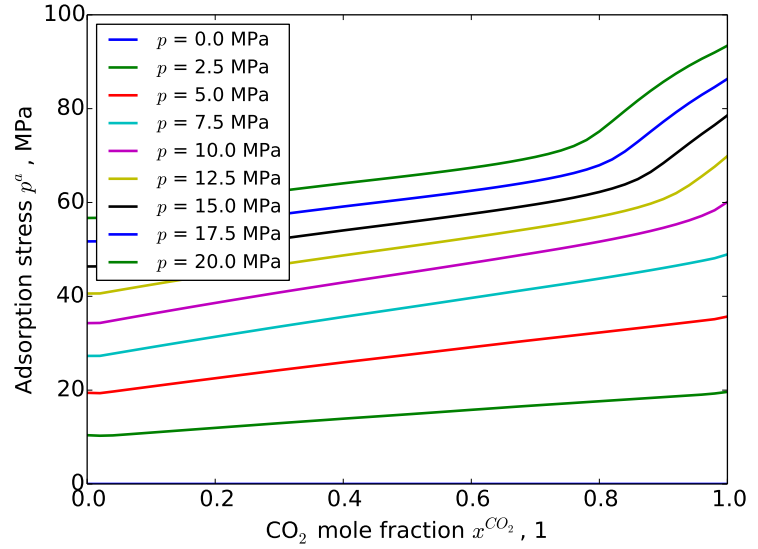


Figure 4: Adsorption stress $s^a(p, x^{\mathrm{CO_2}})$ for Ribolla coal sample exposed to a mixture of methane and carbon dioxide at a temperature $T = 318.15$ K versus (a) the pressure p of the fluid in the cleats and (b) the mole fraction $x^{\mathrm{CO_2}}$ of carbon dioxide in the fluid mixture in the cleats.

a decrease of the porosity ϕ of the cleats: this phenomenon is a direct consequence of the swelling of the coal matrix upon increasing pressure of fluid. In contrast, at a given pressure of the mixture in the cleats, how the porosity of the cleats evolves with the composition of the mixture is non trivial. At the lowest pressures considered, porosity is almost related in an affine manner to the mole fraction $x^{\mathrm{CO_2}}$ of carbon dioxide in the mixture in the cleats. However, at the largest pressures here considered, the relation between porosity and mole fraction becomes significantly nonlinear: at pressures comprised between roughly 15 MPa and 20 MPa, most decrease of the porosity occurs for CO_2 mole fractions greater than 0.8. This behavior reflects the behavior of the adsorption stress as described previously.

After some modification, the state equations (35)-(37) also make it possible to calculate variations of permeability. Indeed, classically for coal, the following stress-based permeability relation is considered [52]:

$$k = k_0 \exp\left(\gamma(\sigma + p)\right) \tag{53}$$

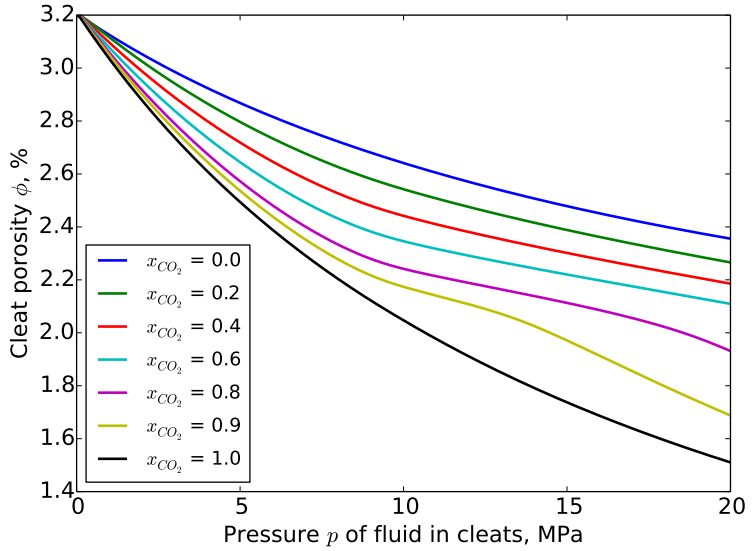
where γ is the so-called pressure sensitivity parameter, first introduced by Brace et al. [53], and where $\sigma + p$ is the Terzaghi's effective stress. Combining this equation with the state equations (35)-(37) enables to find out how permeability is related to the adsorption stress s^a for a representative volume element of coal seam kept in isochoric conditions:

$$k = k_0 \exp\left(\gamma(1-b)(p - s^a)\right) \tag{54}$$

where $b = 1 - K/K_m$ is the Biot coefficient of the coal seam.

Knowing the adsorption stress, this equation makes it possible to calculate

(a)



(b)

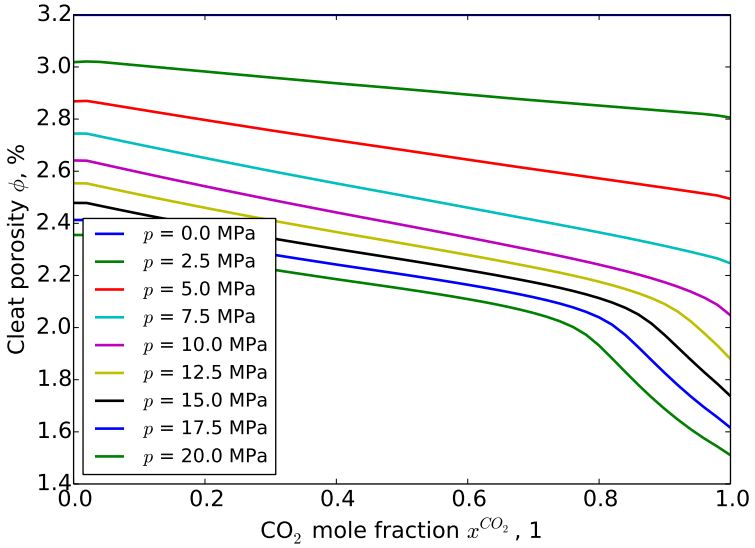


Figure 5: Variations of cleat porosity ϕ of a Ribolla coal sample in isochoric conditions, exposed to a mixture of methane and carbon dioxide at a temperature $T = 318.15$ K versus (a) the pressure p of the fluid in the cleats and (b) the mole fraction $x^{\mathrm{CO_2}}$ of carbon dioxide in the fluid mixture in the cleats.

variations of permeability, as displayed in Fig. 6. One observes that the variations of permeability, when displayed on a logarithmic scale, are very similar to the variations of porosity (see Fig. 5).

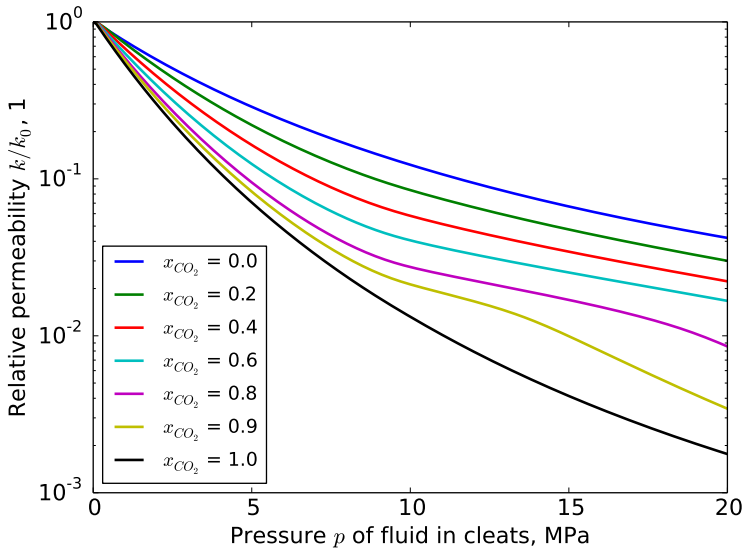
The calculations in this section were performed for a representative volume element in isochoric conditions, which, with free swelling conditions, represent two extreme cases. In free swelling conditions, the model predicts no variation of the Terzaghi's effective stress and thus no variation of permeability. Also, in free swelling conditions, the model predicts a homothetic swelling of the porous solid, from what follows that the pore volume varies such that the Eulerian porosity remains constant.

5.3. Variations of adsorbed amount

In addition to the calculations presented in the previous sections, since the model we propose is fully coupled, predicting the amounts of adsorbed fluids in various conditions is possible. As we will see, taking into account this coupling can lead to significant differences. Here we focus on two identical representative volume elements of coal seam: one element is kept in isochoric conditions, while the other is allowed to swell freely.

Here, in addition to the functions $a^{\mathrm{CH_4}}$ and $a^{\mathrm{CO_2}}$ already calibrated, adsorption isotherms need to be known and calibrated. Again, for the cases of pure fluids, we will use the data of Pini et al. [54], who provide adsorption isotherms of pure methane and pure carbon dioxide on Ribolla coal. Those adsorption isotherms, expressed in terms of total amounts of fluid, are displayed in Fig. 7. By construction, the isotherms provided by Pini et al. converge toward a finite value at infinite pressures, and we therefore interpret them as isotherms representative of isotherms on a rigid coal matrix:

(a)



(b)

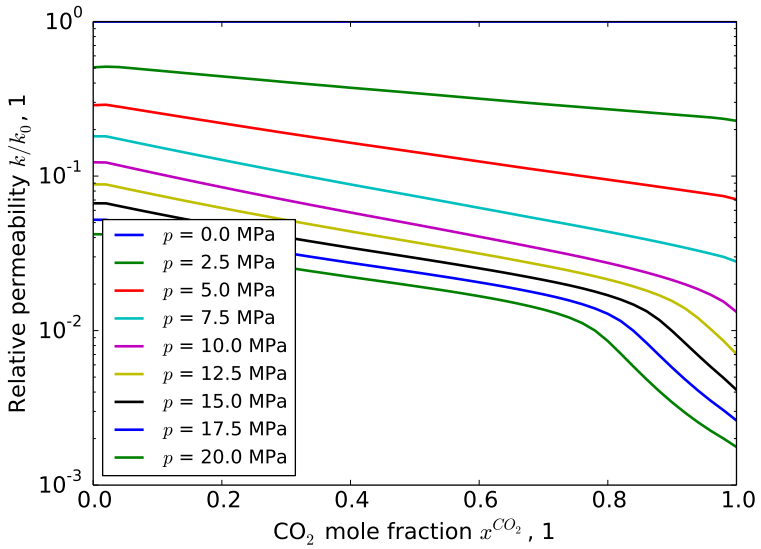


Figure 6: Variations of permeability k of a Ribolla coal sample in isochoric conditions, exposed to a mixture of methane and carbon dioxide at a temperature $T = 318.15$ K versus (a) the pressure p of the fluid in the cleats and (b) the mole fraction $x^{\mathrm{CO_2}}$ of carbon dioxide in the fluid mixture in the cleats.

thus, those isotherms are those noted $n_0^{\mathrm{CH_4}}(p, x^{\mathrm{CO_2}} = 0)$ for pure methane and $n_0^{\mathrm{CO_2}}(p, x^{\mathrm{CO_2}} = 1)$ for pure carbon dioxide.

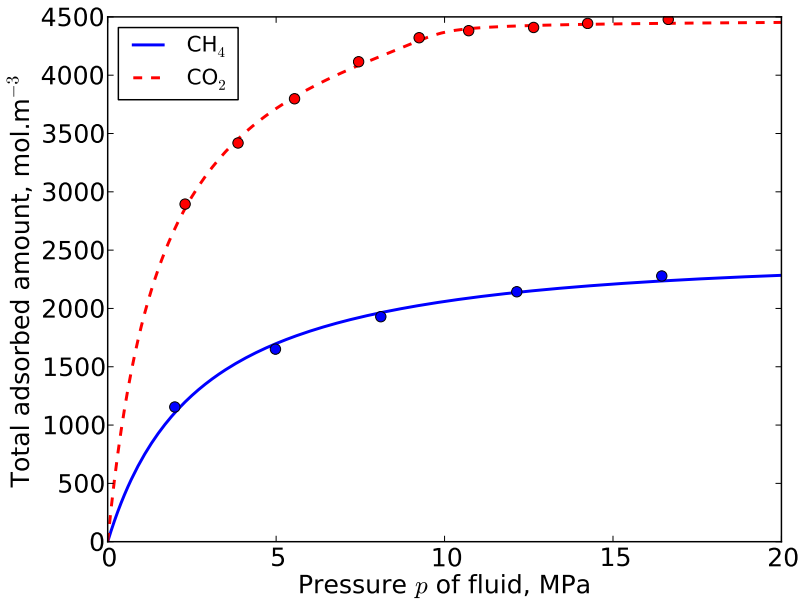


Figure 7: Adsorbed amounts of pure fluids in Ribolla coal at a temperature $T = 318.15$ K, adapted from Pini et al. [54]. Symbols are data points while lines are models fitted by Pini et al. on their data.

In contrast to data of adsorption of pure fluids, data of adsorption of mixtures of fluids are difficult to obtain experimentally, not only because of the complexity of the required experimental setup, but also because of the duration of the corresponding experiments. For our specific problem, as an alternative, we aim at using numerical adsorption isotherms obtained by molecular simulations by Brochard et al. [45]. In particular, Brochard et al. [45] obtained numerical data of adsorbed amounts of both methane

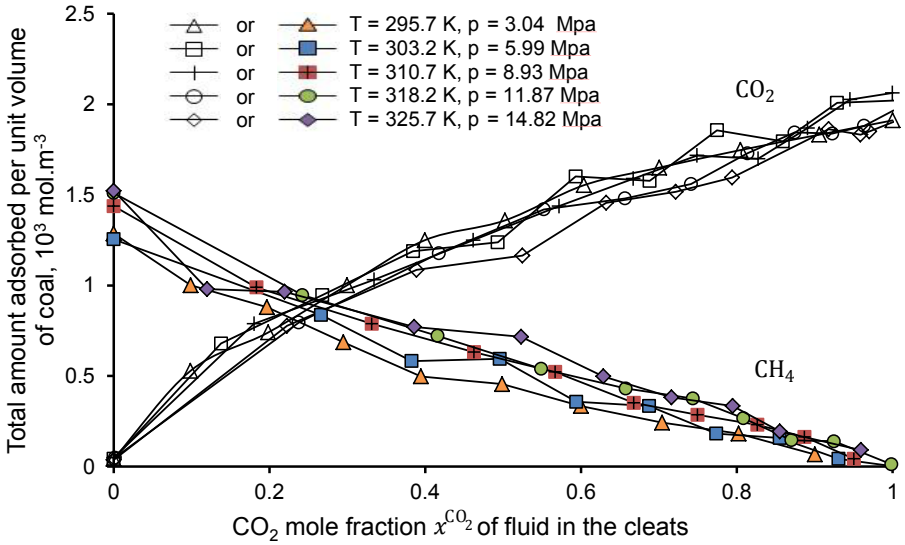


Figure 8: Total amounts of methane and carbon dioxide adsorbed in a rigid coal sample exposed to a mixture of methane and carbon dioxide, adapted from molecular simulations by Brochard et al. [45]. Open symbols are for CO_2 while filled symbols are for CH_4. The CO_2 mole fraction x^{CO_2} is that in a reservoir in thermodynamic equilibrium with the sample (i.e., in our case, of the fluid mixture in the cleats).

and carbon dioxide when a rigid piece of coal matrix is exposed to a mixture of methane and carbon dioxide that contains various mole fractions x^{CO_2} of carbon dioxide, at various temperatures and pressures. Their results are displayed in Fig. 8. From this figure, it appears that the relative amounts of methane and carbon dioxide in the coal matrix depend mostly on the composition of the fluid in thermodynamical equilibrium with the coal matrix. Therefore, we will approximate the mixed adsorption isotherms $n_0^{CH_4}(p, x^{CO_2})$ and $n_0^{CO_2}(p, x^{CO_2})$ by:

$$n_0^{CH_4}(p, x^{CO_2}) = n_0^{CH_4}(p, x^{CO_2} = 0) g^{CH_4}(x^{CO_2}) \tag{55}$$

$$n_0^{CO_2}(p, x^{CO_2}) = n_0^{CO_2}(p, x^{CO_2} = 1) g^{CO_2}(x^{CO_2}) \tag{56}$$

where $n_0^{CH_4}(p, x^{CO_2} = 0)$ and $n_0^{CO_2}(p, x^{CO_2} = 1)$ are the adsorption isotherms of pure methane and pure carbon dioxide on a rigid coal matrix, respectively, and where $g^{CH_4}(x^{CO_2})$ and $g^{CO_2}(x^{CO_2})$ are functions. Those last two functions can readily be obtained from Fig. 8: here those functions are calculated based on the results of Brochard et al. at 318.2 K. Eqs. (55-56) should be considered as the best proposed approximations of the mixed adsorption isotherms that we can make up to now. In absence of any experimental data reported in the literature, these expressions are only supported by results of molecular simulations performed by Brochard et al. [45]. Moreover and unfortunately we were unable to support these approximations by some physical background.

Therefore, making use of Eqs. (27)-(28), the amounts of fluid in the coal matrix can be calculated with:

$$n^{\mathrm{CH_4}}(\epsilon_m, p, x^{\mathrm{CO_2}}) = (1-\phi_0)\left(n_0^{\mathrm{CH_4}}(p, x^{\mathrm{CO_2}}) + a^{\mathrm{CH_4}}(f^{\mathrm{CH_4}})\epsilon_m\right) \tag{57}$$

$$n^{\mathrm{CO_2}}(\epsilon_m, p, x^{\mathrm{CO_2}}) = (1-\phi_0)\left(n_0^{\mathrm{CO_2}}(p, x^{\mathrm{CO_2}}) + a^{\mathrm{CO_2}}(f^{\mathrm{CO_2}})\epsilon_m\right) \tag{58}$$

where the fugacities $f^{\mathrm{CH_4}}$ of methane and $f^{\mathrm{CO_2}}$ of carbon dioxide are given by Eqs. (45)-(46), the functions $a^{\mathrm{CH_4}}$ and $a^{\mathrm{CO_2}}$ by Eqs. (47), and $x^{\mathrm{CO_2}}$ is the CO_2 mole fraction of the fluid in the cleats.

Based on those equations, we calculate the amount of fluid in the coal matrix of a representative volume element of coal seam for two loading paths: the representative volume element is kept in isochoric conditions or is allowed to swell freely. The results of the calculation are displayed in Fig. 9. As expected, for a given composition of mixture, independent of the loading path, increasing the pressure of the fluid in the cleats always increases the total amount of fluid in the coal matrix. Also, one observes that the adsorbed amount depends on the loading path: at the greatest pressure here considered, depending on the composition of the mixture, considering one type of loading or the other can make the total amount of carbon dioxide vary by about 10%. This calculation shows that the effect of deformation on the adsorbed amount must be explicitly taken into account, as our model proposes.

Note finally that the total amount of fluid in the coal seam per unit volume of coal seam (this amount is noted $n_T^{\mathrm{CH_4}}$ for methane and $n_T^{\mathrm{CO_2}}$ for carbon dioxide) is equal to the addition of the amount in the coal matrix with the amount of fluid in the cleats:

$$n_T^{\mathrm{CH_4}} = n^{\mathrm{CH_4}} + \rho^{\mathrm{CH_4}}\phi \text{ and } n_T^{\mathrm{CO_2}} = n^{\mathrm{CO_2}} + \rho^{\mathrm{CO_2}}\phi. \tag{59}$$

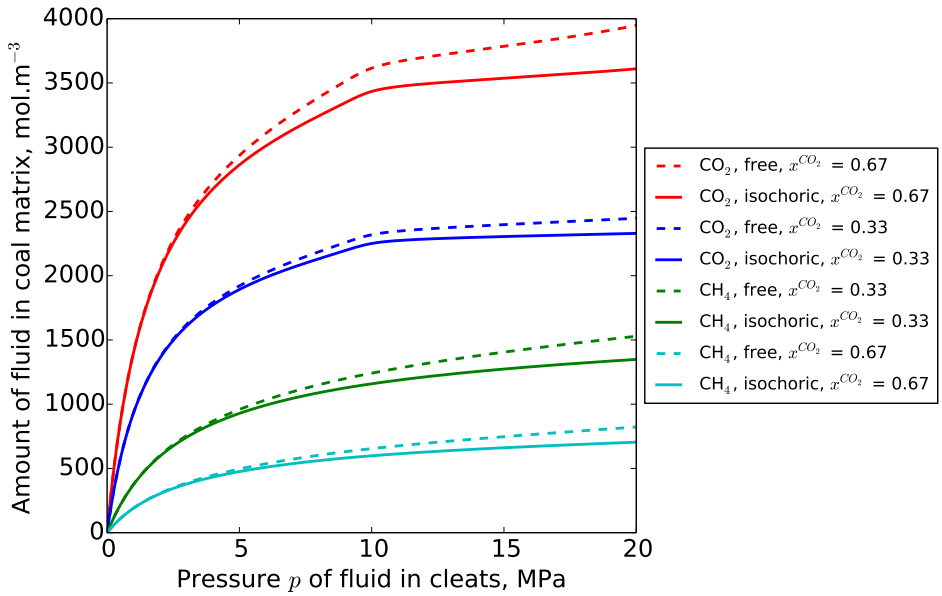


Figure 9: Predicted amounts of methane and carbon dioxide in the coal matrix, for a representative volume element of coal seam injected with a binary mixture of fluids with various compositions and pressures, and kept in isochoric conditions or allowed to swell freely.

where ρ^{CH_4} and ρ^{CO_2} are the bulk densities of methane and carbon dioxide, respectively.

6. Concluding remarks

In this work, the poromechanical model derived in Nikoosokhan et al. [44] for coal exposed to a pure fluid was extended to coal exposed to a binary mixture. Some assumptions were needed in order to obtain a thermodynamically consistent model that could be fully calibrated with available data. Those assumptions are on the consideration of small strains (see Eqs. (27)-(28)), on the shape of the adsorption isotherms of mixtures (see Eqs. (55)-(56)), and on the dependency of the introduced functions a^{CH_4} and a^{CO_2} (see Eqs. (43)-(44)) on the fugacities of the fluids in the mixture.

We showed that calculating permeability and porosity evolutions only required data of adsorption-induced swellings in presence of pure fluids for the model to be calibrated. In contrast, calculating adsorbed amounts on deformed samples required to know data of adsorption-induced swellings with pure fluids and isotherms of adsorption and co-adsorption. Here we used swelling data and adsorption data with pure fluids obtained experimentally, while we used data obtained by molecular simulations for the co-adsorption isotherms (see Figs. 3a and 7).

One feature of our model is that it captures the full coupling between adsorption and stress/strain: not only does it model the fact that adsorption generates adsorption stresses (or strains), but also does it model the fact that adsorption is modified by the stresses or strains to which the solid is subjected. By performing calculations on a representative volume element

of coal seam exposed to a binary mixture of methane with carbon dioxide, we showed that, when taking into account this second coupling, predicted amounts of adsorbed fluids depend on the loading path to which the representative volume element is submitted.

Deriving the state equations (35)-(38) in a thermodynamically consistent manner and making sure that those equations could be fully calibrated was a first step toward an implementation in a finite-element code and the numerical modeling of a full CO_2-Enhanced Coal Bed Methane (CO_2-ECBM) recovery process.

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